

**ORGANOPHOTORECEPTOR WITH A CHARGE TRANSPORT MATERIAL
HAVING TWO HYDRAZONE GROUPS**

CROSS REFERENCE TO RELATED APPLICATION

This application claims priority to copending U.S. Provisional Patent Application
5 serial number 60/451,308 to Tokarski et al., entitled "Organophotoreceptor With Novel
Charge Transport Material," incorporated herein by reference.

FIELD OF THE INVENTION

This invention relates to organophotoreceptors suitable for use in
10 electrophotography and, more specifically, to organophotoreceptors having a desirable
charge transport material with two hydrazone groups and two amino groups.

BACKGROUND OF THE INVENTION

In electrophotography, an organophotoreceptor in the form of a plate, disk, sheet,
15 belt, drum or the like having an electrically insulating photoconductive element on an
electrically conductive substrate is imaged by first uniformly electrostatically charging
the surface of the photoconductive layer, and then exposing the charged surface to a
pattern of light. The light exposure selectively dissipates the charge in the illuminated
areas where light strikes the surface, thereby forming a pattern of charged and uncharged
20 areas, referred to as a latent image. A liquid or solid toner is then provided in the vicinity
of the latent image, and toner droplets or particles deposit in the vicinity of either the
charged or uncharged areas to create a toned image on the surface of the photoconductive
layer. The resulting toned image can be transferred to a suitable ultimate or intermediate
receiving surface, such as paper, or the photoconductive layer can operate as an ultimate
25 receptor for the image. The imaging process can be repeated many times to complete a
single image, for example, by overlaying images of distinct color components or effect
shadow images, such as overlaying images of distinct colors to form a full color final
image, and/or to reproduce additional images.

Both single layer and multilayer photoconductive elements have been used. In
30 single layer embodiments, a charge transport material and charge generating material are
combined with a polymeric binder and then deposited on the electrically conductive

substrate. In multilayer embodiments, the charge transport material and charge generating material are present in the element in separate layers, each of which can optionally be combined with a polymeric binder, deposited on the electrically conductive substrate. Two arrangements are possible for a two-layer photoconductive element. In

5 one two-layer arrangement (the "dual layer" arrangement), the charge-generating layer is deposited on the electrically conductive substrate and the charge transport layer is deposited on top of the charge generating layer. In an alternate two-layer arrangement (the "inverted dual layer" arrangement), the order of the charge transport layer and charge generating layer is reversed.

10 In both the single and multilayer photoconductive elements, the purpose of the charge generating material is to generate charge carriers (i.e., holes and/or electrons) upon exposure to light. The purpose of the charge transport material is to accept at least one type of these charge carriers and transport them through the charge transport layer in order to facilitate discharge of a surface charge on the photoconductive element. The

15 charge transport material can be a charge transport compound, an electron transport compound, or a combination of both. When a charge transport compound is used, the charge transport compound accepts the hole carriers and transports them through the layer with the charge transport compound. When an electron transport compound is used, the electron transport compound accepts the electron carriers and transports them through

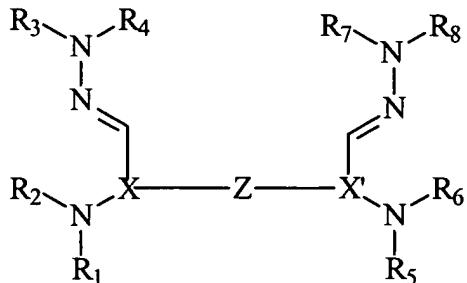
20 the layer with the electron transport compound.

SUMMARY OF THE INVENTION

This invention provides organophotoreceptors having good electrostatic properties such as high V_{acc} and low V_{dis} .

25 In a first aspect, an organophotoreceptor comprises an electrically conductive substrate and a photoconductive element on the electrically conductive substrate, the photoconductive element comprising:

(a) a charge transport material having the formula



where R₁, R₂, R₃, R₄, R₅, R₆, R₇, and R₈ are, each independently, an alkyl group, an alkaryl group, an aryl group, or heterocyclic group, X and X' are, each independently, aromatic groups, and Z is a divalent linking group having the formula -(CH₂)_m- , branched or linear, where m is an integer between 1 and 30, inclusive, and one or more of the methylene groups may be replaced by O, S, C=O, O=S=O, a heterocyclic group, an aromatic group, urethane, urea, an ester group, a NR₉ group, a CHR₁₀ group, or a CR₁₁R₁₂ group where R₉ and R₁₀ are, each independently, H, hydroxyl, thiol, an alkoxy group, an alkyl group, or an aryl group, and R₁₁, and R₁₂ are, each independently, H, hydroxyl, thiol, an alkoxy group, an alkyl group, an aryl group, or a part of a cyclic ring; and

(b) a charge generating compound.

The organophotoreceptor may be provided, for example, in the form of a plate, a flexible belt, a flexible disk, a sheet, a rigid drum, or a sheet around a rigid or compliant drum. In one embodiment, the organophotoreceptor includes: (a) a photoconductive element comprising the charge transport material, the charge generating compound, a second charge transport material, and a polymeric binder; and (b) the electrically conductive substrate.

In a second aspect, the invention features an electrophotographic imaging apparatus that comprises (a) a light imaging component; and (b) the above-described organophotoreceptor oriented to receive light from the light imaging component. The apparatus can further comprise a toner dispenser, such as a liquid toner dispenser. The method of electrophotographic imaging with photoreceptors containing the above noted charge transport materials is also described.

In a third aspect, the invention features an electrophotographic imaging process that includes (a) applying an electrical charge to a surface of the above-described

organophotoreceptor; (b) imagewise exposing the surface of the organophotoreceptor to radiation to dissipate charge in selected areas and thereby form a pattern of at least relatively charged and uncharged areas on the surface; (c) contacting the surface with a toner, such as a liquid toner that includes a dispersion of colorant particles in an organic liquid, to create a toned image; and (d) transferring the toned image to a substrate.

In a fourth aspect, the invention features a charge transport material having the general formula above.

The invention provides suitable charge transport materials for organophotoreceptors featuring a combination of good mechanical and electrostatic properties. These photoreceptors can be used successfully with liquid toners to produce high quality images. The high quality of the imaging system can be maintained after repeated cycling.

Other features and advantages of the invention will be apparent from the following description of the particular embodiments thereof, and from the claims.

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DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

An organophotoreceptor as described herein has an electrically conductive substrate and a photoconductive element comprising a charge generating compound and a charge transport material having two aromatic groups linked by a linking group where each of the aromatic group, each independently, is bonded to both a hydrazone group and an amino group. These charge transport materials have desirable properties as evidenced by their performance in organophotoreceptors for electrophotography. In particular, the charge transport materials of this invention have high charge carrier mobilities and good compatibility with various binder materials, and possess excellent electrophotographic properties. The organophotoreceptors according to this invention generally have a high photosensitivity, a low residual potential, and a high stability with respect to cycle testing, crystallization, and organophotoreceptor bending and stretching. The organophotoreceptors are particularly useful in laser printers and the like as well as fax machines, photocopies, scanners and other electronic devices based on electrophotography. The use of these charge transport materials is described in more

detail below in the context of laser printer use, although their application in other devices operating by electrophotography can be generalized from the discussion below.

To produce high quality images, particularly after multiple cycles, it is desirable for the charge transport materials to form a homogeneous solution with the polymeric binder and remain approximately homogeneously distributed through the organophotoreceptor material during the cycling of the material. In addition, it is desirable to increase the amount of charge that the charge transport material can accept (indicated by a parameter known as the acceptance voltage or "V_{acc}"), and to reduce retention of that charge upon discharge (indicated by a parameter known as the discharge voltage or "V_{dis}").

The charge transport materials can be classified as a charge transport compound or an electron transport compound. There are many charge transport compounds and electron transport compounds known in the art for electrophotography. Non-limiting examples of charge transport compounds include, for example, pyrazoline derivatives, fluorene derivatives, oxadiazole derivatives, stilbene derivatives, enamine derivatives, enamine stilbene derivatives, hydrazone derivatives, carbazole hydrazone derivatives, (N,N-disubstituted)arylamines such as triaryl amines, polyvinyl carbazole, polyvinyl pyrene, polyacenaphthylene, or multi-hydrazone compounds comprising at least two hydrazone groups and at least two groups selected from the group consisting of (N,N-disubstituted)arylamine such as triphenylamine and heterocycles such as carbazole, julolidine, phenothiazine, phenazine, phenoxazine, phenoxathiin, thiazole, oxazole, isoxazole, dibenzo(1,4)dioxin, thianthrene, imidazole, benzothiazole, benzotriazole, benzoxazole, benzimidazole, quinoline, isoquinoline, quinoxaline, indole, indazole, pyrrole, purine, pyridine, pyridazine, pyrimidine, pyrazine, triazole, oxadiazole, tetrazole, thiadiazole, benzisoxazole, benzisothiazole, dibenzofuran, dibenzothiophene, thiophene, thianaphthene, quinazoline, or cinnoline.

Non-limiting examples of electron transport compounds include, for example, bromoaniline, tetracyanoethylene, tetracyanoquinodimethane, 2,4,7-trinitro-9-fluorenone, 2,4,5,7-tetranitro-9-fluorenone, 2,4,5,7-tetranitroxanthone, 2,4,8-trinitrothioxanthone, 2,6,8-trinitro-indeno[1,2-b]thiophene-4-one, and 1,3,7-trinitrobibenzo thiophene-5,5-dioxide, (2,3-diphenyl-1-indenylidene)malononitrile, 4H-thiopyran-1,1-dioxide and its

derivatives such as 4-dicyanomethylene-2,6-diphenyl-4H-thiopyran-1,1-dioxide, 4-dicyanomethylene-2,6-di-m-tolyl-4H-thiopyran-1,1-dioxide, and unsymmetrically substituted 2,6-diaryl-4H-thiopyran-1,1-dioxide such as 4H-1,1-dioxo-2-(p-isopropylphenyl)-6-phenyl-4-(dicyanomethylidene)thiopyran and 4H-1,1-dioxo-2-(p-isopropylphenyl)-6-(2-thienyl)-4-(dicyanomethylidene)thiopyran, derivatives of phospha-2,5-cyclohexadiene, alkoxy carbonyl-9-fluorenylidene)malononitrile derivatives such as (4-n-butoxycarbonyl-9-fluorenylidene)malononitrile, (4-phenethoxycarbonyl-9-fluorenylidene)malononitrile, (4-carboxy-9-fluorenylidene)malononitrile, and diethyl(4-n-butoxycarbonyl-2,7-dinitro-9-fluorenylidene)malonate, anthraquinodimethane derivatives such as 11,11,12,12-tetracyano-2-alkylanthraquinodimethane and 11,11-dicyano-12,12-bis(ethoxycarbonyl)anthraquinodimethane, anthrone derivatives such as 1-chloro-10-[bis(ethoxycarbonyl)methylene]anthrone, 1,8-dichloro-10-[bis(ethoxy carbonyl) methylene]anthrone, 1,8-dihydroxy-10-[bis(ethoxycarbonyl)methylene]anthrone, and 1-cyano-10-[bis(ethoxycarbonyl)methylene]anthrone, 7-nitro-2-aza-9-fluroenylidene-malononitrile, diphenoquinone derivatives, benzoquinone derivatives, naphtoquinone derivatives, quinine derivatives, tetracyanoethylenecyanoethylene, 2,4,8-trinitro thioxantone, dinitrobenzene derivatives, dinitroanthracene derivatives, dinitroacridine derivatives, nitroanthraquinone derivatives, dinitroanthraquinone derivatives, succinic anhydride, maleic anhydride, dibromo maleic anhydride, pyrene derivatives, carbazole derivatives, hydrazone derivatives, N,N-dialkylaniline derivatives, diphenylamine derivatives, triphenylamine derivatives, triphenylmethane derivatives, tetracyano quinodimethane, 2,4,5,7-tetranitro-9-fluorenone, 2,4,7-trinitro-9-dicyanomethylene fluorenone, 2,4,5,7-tetranitroxanthone derivatives, and 2,4,8-trinitrothioxanthone derivatives. In some embodiments of interest, the electron transport compound comprises an (alkoxycarbonyl-9-fluorenylidene)malononitrile derivative, such as (4-n-butoxycarbonyl-9-fluorenylidene)malononitrile.

Although there are many charge transport materials available, there is a need for other charge transport materials to meet the various requirements of particular electrophotography applications.

In electrophotography applications, a charge-generating compound within an organophotoreceptor absorbs light to form electron-hole pairs. These electrons and holes

can be transported over an appropriate time frame under a large electric field to discharge locally a surface charge that is generating the field. The discharge of the field at a particular location results in a surface charge pattern that essentially matches the pattern drawn with the light. This charge pattern then can be used to guide toner deposition. The
5 charge transport materials described herein are especially effective at transporting charge, and in particular holes from the electron-hole pairs formed by the charge generating compound. In some embodiments, a specific electron transport compound or charge transport compound can also be used along with the charge transport material of this invention.

10 The layer or layers of materials containing the charge generating compound and the charge transport materials are within an organophotoreceptor. To print a two dimensional image using the organophotoreceptor, the organophotoreceptor has a two dimensional surface for forming at least a portion of the image. The imaging process then continues by cycling the organophotoreceptor to complete the formation of the entire
15 image and/or for the processing of subsequent images.

The organophotoreceptor may be provided in the form of a plate, a flexible belt, a disk, a rigid drum, a sheet around a rigid or compliant drum, or the like. The charge transport material can be in the same layer as the charge generating compound and/or in a different layer from the charge generating compound. Additional layers can be used also,
20 as described further below.

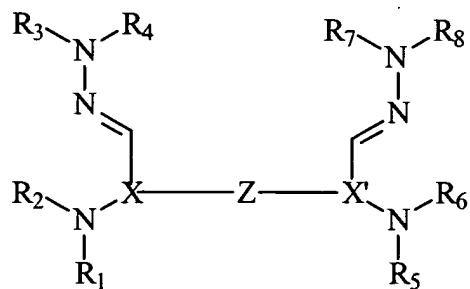
In some embodiments, the organophotoreceptor material comprises, for example:
(a) a charge transport layer comprising the charge transport material and a polymeric binder; (b) a charge generating layer comprising the charge generating compound and a polymeric binder; and (c) the electrically conductive substrate. The charge transport
25 layer may be intermediate between the charge generating layer and the electrically conductive substrate. Alternatively, the charge generating layer may be intermediate between the charge transport layer and the electrically conductive substrate. In further embodiments, the organophotoreceptor material has a single layer with both a charge transport material and a charge generating compound within a polymeric binder.

30 The organophotoreceptors can be incorporated into an electrophotographic imaging apparatus, such as laser printers. In these devices, an image is formed from

physical embodiments and converted to a light image that is scanned onto the organophotoreceptor to form a surface latent image. The surface latent image can be used to attract toner onto the surface of the organophotoreceptor, in which the toner image is the same or the negative of the light image projected onto the organophotoreceptor. The toner can be a liquid toner or a dry toner. The toner is subsequently transferred, from the surface of the organophotoreceptor, to a receiving surface, such as a sheet of paper. After the transfer of the toner, the surface is discharged, and the material is ready to cycle again. The imaging apparatus can further comprise, for example, a plurality of support rollers for transporting a paper receiving medium and/or for movement of the photoreceptor, a light imaging component with suitable optics to form the light image, a light source, such as a laser, a toner source and delivery system and an appropriate control system.

An electrophotographic imaging process generally can comprise (a) applying an electrical charge to a surface of the above-described organophotoreceptor; (b) imagewise exposing the surface of the organophotoreceptor to radiation to dissipate charge in selected areas and thereby form a pattern of charged and uncharged areas on the surface; (c) exposing the surface with a toner, such as a liquid toner that includes a dispersion of colorant particles in an organic liquid to create a toner image, to attract toner to the charged or discharged regions of the organophotoreceptor; and (d) transferring the toner image to a substrate.

As described herein, an organophotoreceptor comprises a charge transport material having the formula



where R₁, R₂, R₃, R₄, R₅, R₆, R₇, and R₈ are, each independently, an alkyl group,
an alkaryl group, an aryl group, or heterocyclic group, X and X' are, each independently,
aromatic groups, and Z is a divalent linking group having the formula -(CH₂)_m- , branched

or linear, where m is an integer between 1 and 30, inclusive, and one or more of the methylene groups may be replaced by O, S, C=O, O=S=O, a heterocyclic group, an aromatic group, urethane, urea, an ester group, a NR₉ group, a CHR₁₀ group, or a CR₁₁R₁₂ group where R₉ and R₁₀ are, each independently, H, hydroxyl, thiol, an alkoxy group, an alkyl group, or an aryl group, and R₁₁, and R₁₂ are, each independently, H, hydroxyl, thiol, an alkoxy group, an alkyl group, an aryl group, or a part of a cyclic ring.

The aromatic group can be any conjugated system containing $4n + 2 \pi$ -electrons. There are many criteria available for determining aromaticity. A widely employed criterion for the quantitative assessment of aromaticity is the resonance energy. In general, the resonance energy of the aromatic group is greater than 10 KJ/mol. Aromatic groups may be classified as aromatic heterocyclic group which contains at least a heteroatom in the $4n + 2 \pi$ -electron ring, and aryl group which does not contain a heteroatom in the $4n + 2 \pi$ -electron ring. Nonetheless, both the aromatic heterocyclic and the aryl group may have at least one heteroatom in a substituent attached to the $4n + 2 \pi$ -electron ring. Furthermore, both the aromatic heterocyclic and the aryl group may include monocyclic, bicyclic, and polycyclic aromatic rings.

Non-limiting examples of the aromatic heterocyclic group are furanyl, thiophenyl, pyrrolyl, indolyl, carbazolyl, benzofuranyl, benzothiophenyl, dibenzofuranyl, dibenzothiophenyl, pyridinyl, pyridazinyl, pyrimidinyl, pyrazinyl, triazinyl, tetrazinyl, petazinyl, quinolinyl, isoquinolinyl, cinnolinyl, phthalazinyl, quinazolinyl, quinoxalinyl, naphthyridinyl, pteridinyl, acridinyl, phenanthridinyl, phenanthrolinyl, anthyridinyl, purinyl, pteridinyl, alloxazinyl, phenazinyl, phenothiazinyl, phenoxazinyl, phenoxathiinyl, dibenzo(1,4)dioxinyl, thianthrenyl, and a combination thereof. The aromatic heterocyclic group may also include any combination of the above aromatic heterocyclic groups bonded together either by a bond (as in bicarbazolyl) or by a linking group (as in 1,6-di(10H-10-phenothiazinyl)hexane). The linking group may include an aliphatic group, aromatic group, or a combination thereof. Furthermore, both the aliphatic group and aromatic group may contain at least a heteroatom such as O, S, and N.

Non-limiting examples of the aryl group are phenyl, naphthyl, benzyl, or tolanyl group, sexiphenylene, phenanthrenyl, anthracenyl, coronenyl, and tolanylphenyl. The aryl group may also include any combination of the above aryl groups bonded together

by either a bond (as in biphenyl group) or a linking group (as in stilbenyl, diphenyl sulfone, an arylamine group). The linking group may include an aliphatic group, aromatic group, or a combination thereof. Furthermore, both the aliphatic group and aromatic group may contain at least a heteroatom such as O, S, and N.

5 Substitution is liberally allowed on the chemical groups to affect various physical effects on the properties of the compounds, such as mobility, sensitivity, solubility, compatibility, stability, and the like, as is known generally in the art. In the description of chemical substituents, there are certain practices common to the art that are reflected in the use of language. The term group indicates that the generically recited chemical entity
10 (e.g., alkyl group, alkenyl group, aryl group, aromatic group, heterocyclic group, etc.) may have any substituent thereon which is consistent with the bond structure of that group. For example, where the term 'alkyl group' is used, that term would not only include unsubstituted linear, branched and cyclic alkyls, such as methyl, ethyl, isopropyl, tert-butyl, cyclohexyl, dodecyl and the like, but also substituents having heteroatom such
15 as 3-ethoxylpropyl, 4-(N-ethylamino)butyl, 3-hydroxypentyl, 2-thiolhexyl, 1,2,3-tribromoopropyl, and the like. However, as is consistent with such nomenclature, no substitution would be included within the term that would alter the fundamental bond structure of the underlying group. For example, where a phenyl group is recited, substitution such as 1-aminophenyl, 2,4-dihydroxyphenyl, 1,3,5-trithiophenyl, 1,3,5-
20 trimethoxyphenyl and the like would be acceptable within the terminology, while substitution of 1,1,2,2,3,3-hexamethylphenyl would not be acceptable as that substitution would require the ring bond structure of the phenyl group to be altered to a non-aromatic form because of the substitution. When referring to an aromatic group, the substituent cited will include any substitution that does not decrease the resonance energy of the
25 aromatic group to less than 10 KJ/mol. Where the term moiety is used, such as alkyl moiety or phenyl moiety, that terminology indicates that the chemical moiety is not substituted. When referring to an alkyl moiety, the term represents only an unsubstituted alkyl hydrocarbon group, whether branched, straight chain, or cyclic and whether saturated or unsaturated.

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Organophotoreceptors

The organophotoreceptor may be, for example, in the form of a plate, a sheet, a flexible belt, a disk, a rigid drum, or a sheet around a rigid or compliant drum, with flexible belts and rigid drums generally being used in commercial embodiments. The organophotoreceptor may comprise, for example, an electrically conductive substrate and

5 on the electrically conductive substrate a photoconductive element in the form of one or more layers. The photoconductive element can comprise both a charge transport material and a charge generating compound in a polymeric binder, which may or may not be in the same layer, as well as a second charge transport material such as a charge transport compound or an electron transport compound in some embodiments. For example, the

10 charge transport material and the charge generating compound can be in a single layer. In other embodiments, however, the photoconductive element comprises a bilayer construction featuring a charge generating layer and a separate charge transport layer. The charge generating layer may be located intermediate between the electrically conductive substrate and the charge transport layer. Alternatively, the photoconductive

15 element may have a structure in which the charge transport layer is intermediate between the electrically conductive substrate and the charge generating layer.

The electrically conductive substrate may be flexible, for example in the form of a flexible web or a belt, or inflexible, for example in the form of a drum. A drum can have a hollow cylindrical structure that provides for attachment of the drum to a drive that

20 rotates the drum during the imaging process. Typically, a flexible electrically conductive substrate comprises an electrically insulating substrate and a thin layer of electrically conductive material onto which the photoconductive material is applied.

The electrically insulating substrate may be paper or a film forming polymer such as polyester (e.g., polyethylene terephthalate or polyethylene naphthalate), polyimide,

25 polysulfone, polypropylene, nylon, polyester, polycarbonate, polyvinyl resin, polyvinyl fluoride, polystyrene and the like. Specific examples of polymers for supporting substrates included, for example, polyethersulfone (StabarTM S-100, available from ICI), polyvinyl fluoride (Tedlar[®], available from E.I. DuPont de Nemours & Company), polybisphenol-A polycarbonate (MakrofolTM, available from Mobay Chemical Company)

30 and amorphous polyethylene terephthalate (MelinarTM, available from ICI Americas, Inc.). The electrically conductive materials may be graphite, dispersed carbon black,

iodine, conductive polymers such as polypyrroles and Calgon® conductive polymer 261 (commercially available from Calgon Corporation, Inc., Pittsburgh, Pa.), metals such as aluminum, titanium, chromium, brass, gold, copper, palladium, nickel, or stainless steel, or metal oxide such as tin oxide or indium oxide. In embodiments of particular interest,

5 the electrically conductive material is aluminum. Generally, the photoconductor substrate has a thickness adequate to provide the required mechanical stability. For example, flexible web substrates generally have a thickness from about 0.01 to about 1 mm, while drum substrates generally have a thickness from about 0.5 mm to about 2 mm.

10 The charge generating compound is a material that is capable of absorbing light to generate charge carriers, such as a dye or pigment. Non-limiting examples of suitable charge generating compounds include, for example, metal-free phthalocyanines (e.g., ELA 8034 metal-free phthalocyanine available from H.W. Sands, Inc. or Sanyo Color Works, Ltd., CGM-X01), metal phthalocyanines such as titanium phthalocyanine, copper

15 phthalocyanine, oxytitanium phthalocyanine (also referred to as titanyl oxyphthalocyanine, and including any crystalline phase or mixtures of crystalline phases that can act as a charge generating compound), hydroxygallium phthalocyanine, squarylium dyes and pigments, hydroxy-substituted squarylium pigments, perylimides, polynuclear quinones available from Allied Chemical Corporation under the trade name

20 Indofast® Double Scarlet, Indofast® Violet Lake B, Indofast® Brilliant Scarlet and Indofast® Orange, quinacridones available from DuPont under the trade name Monastral™ Red, Monastral™ Violet and Monastral™ Red Y, naphthalene 1,4,5,8-tetracarboxylic acid derived pigments including the perinones, tetrabenzoporphyrins and tetranaphthaloporphyrins, indigo- and thioindigo dyes, benzothioxanthene-derivatives,

25 perylene 3,4,9,10-tetracarboxylic acid derived pigments, polyazo-pigments including bisazo-, trisazo- and tetrakisazo-pigments, polymethine dyes, dyes containing quinazoline groups, tertiary amines, amorphous selenium, selenium alloys such as selenium-tellurium, selenium-tellurium-arsenic and selenium-arsenic, cadmium sulphoselenide, cadmium selenide, cadmium sulphide, and mixtures thereof. For some embodiments, the charge

30 generating compound comprises oxytitanium phthalocyanine (e.g., any phase thereof), hydroxygallium phthalocyanine or a combination thereof.

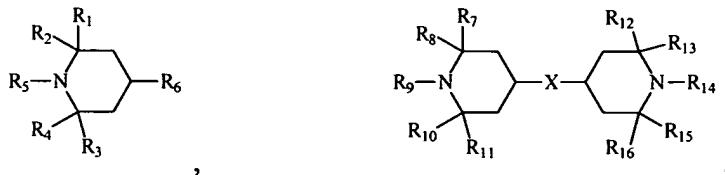
The photoconductive layer of this invention may optionally contain a second charge transport material which may be a charge transport compound, an electron transport compound, or a combination of both. Generally, any charge transport compound or electron transport compound known in the art can be used as the second
5 charge transport material.

An electron transport compound and a UV light stabilizer can have a synergistic relationship for providing desired electron flow within the photoconductor. The presence of the UV light stabilizers alters the electron transport properties of the electron transport compounds to improve the electron transporting properties of the composite. UV light
10 stabilizers can be ultraviolet light absorbers or ultraviolet light inhibitors that trap free radicals.

UV light absorbers can absorb ultraviolet radiation and dissipate it as heat. UV light inhibitors are thought to trap free radicals generated by the ultraviolet light and after trapping of the free radicals, subsequently to regenerate active stabilizer moieties with
15 energy dissipation. In view of the synergistic relationship of the UV stabilizers with electron transport compounds, the particular advantages of the UV stabilizers may not be their UV stabilizing abilities, although the UV stabilizing ability may be further advantageous in reducing degradation of the organophotoreceptor over time. The improved synergistic performance of organophotoreceptors with layers comprising both
20 an electron transport compound and a UV stabilizer are described further in copending U.S. Patent Application Serial Number 10/425,333 filed on April 28, 2003 to Zhu, entitled "Organophotoreceptor With A Light Stabilizer," incorporated herein by reference.

Non-limiting examples of suitable light stabilizer include, for example, hindered trialkylamines such as Tinuvin 144 and Tinuvin 292 (from Ciba Specialty Chemicals,
25 Terrytown, NY), hindered alkoxydialkylamines such as Tinuvin 123 (from Ciba Specialty Chemicals), benzotriazoles such as Tinuvan 328, Tinuvin 900 and Tinuvin 928 (from Ciba Specialty Chemicals), benzophenones such as Sanduvor 3041 (from Clariant Corp., Charlotte, N.C.), nickel compounds such as Arbestab (from Robinson Brothers Ltd, West Midlands, Great Britain), salicylates, cyanocinnamates, benzylidene malonates,
30 benzoates, oxanilides such as Sanduvor VSU (from Clariant Corp., Charlotte, N.C.), triazines such as Cyagard UV-1164 (from Cytec Industries Inc., N.J.), polymeric

sterically hindered amines such as Luchem (from Atochem North America, Buffalo, NY). In some embodiments, the light stabilizer is selected from the group consisting of hindered trialkylamines having the following formula:



5 where R₁, R₂, R₃, R₄, R₆, R₇, R₈, R₁₀, R₁₁, R₁₂, R₁₃, R₁₄, R₁₅ are, each independently, hydrogen, alkyl group, or ester, or ether group; and R₅, R₉, and R₁₄ are, each independently, alkyl group; and X is a linking group selected from the group consisting of -O-CO-(CH₂)_m-CO-O- where m is between 2 to 20.

The binder generally is capable of dispersing or dissolving the charge transport material (in the case of the charge transport layer or a single layer construction), the charge generating compound (in the case of the charge generating layer or a single layer construction) and/or an electron transport compound for appropriate embodiments. Examples of suitable binders for both the charge generating layer and charge transport layer generally include, for example, polystyrene-co-butadiene, polystyrene-co-acrylonitrile, modified acrylic polymers, polyvinyl acetate, styrene-alkyd resins, soya-alkyl resins, polyvinylchloride, polyvinylidene chloride, polyacrylonitrile, polycarbonates, polyacrylic acid, polyacrylates, polymethacrylates, styrene polymers, polyvinyl butyral, alkyd resins, polyamides, polyurethanes, polyesters, polysulfones, polyethers, polyketones, phenoxy resins, epoxy resins, silicone resins, polysiloxanes, poly(hydroxyether) resins, polyhydroxystyrene resins, novolak, poly(phenylglycidyl ether)-co-dicyclopentadiene, copolymers of monomers used in the above-mentioned polymers, and combinations thereof. Specific suitable binders include, for example, polyvinyl butyral, polycarbonate, and polyester. Non-limiting examples of polyvinyl butyral include BX-1 and BX-5 from Sekisui Chemical Co. Ltd., Japan. Non-limiting examples of suitable polycarbonate include polycarbonate A which is derived from bisphenol-A (e.g. Iupilon-A from Mitsubishi Engineering Plastics, or Lexan 145 from General Electric); polycarbonate Z which is derived from cyclohexylidene bisphenol (e.g. Iupilon-Z from Mitsubishi Engineering Plastics Corp, White Plain, New York); and polycarbonate C which is derived from methylbisphenol A (from Mitsubishi Chemical

Corporation). Non-limiting examples of suitable polyester binders include ortho-polyethylene terephthalate (e.g. OPET TR-4 from Kanebo Ltd., Yamaguchi, Japan).

Suitable optional additives for any one or more of the layers include, for example, antioxidants, coupling agents, dispersing agents, curing agents, surfactants, and
5 combinations thereof.

The photoconductive element overall typically has a thickness from about 10 microns to about 45 microns. In the dual layer embodiments having a separate charge generating layer and a separate charge transport layer, charge generation layer generally has a thickness from about 0.5 microns to about 2 microns, and the charge transport layer
10 has a thickness from about 5 microns to about 35 microns. In embodiments in which the charge transport material and the charge generating compound are in the same layer, the layer with the charge generating compound and the charge transport composition generally has a thickness from about 7 microns to about 30 microns. In embodiments with a distinct electron transport layer, the electron transport layer has an average
15 thickness from about 0.5 microns to about 10 microns and in further embodiments from about 1 micron to about 3 microns. In general, an electron transport overcoat layer can increase mechanical abrasion resistance, increases resistance to carrier liquid and atmospheric moisture, and decreases degradation of the photoreceptor by corona gases. A person of ordinary skill in the art will recognize that additional ranges of thickness
20 within the explicit ranges above are contemplated and are within the present disclosure.

Generally, for the organophotoreceptors described herein, the charge generation compound is in an amount from about 0.5 to about 25 weight percent, in further embodiments in an amount from about 1 to about 15 weight percent, and in other embodiments in an amount from about 2 to about 10 weight percent, based on the weight
25 of the photoconductive layer. The charge transport material is in an amount from about 10 to about 80 weight percent, based on the weight of the photoconductive layer, in further embodiments in an amount from about 35 to about 60 weight percent, and in other embodiments from about 45 to about 55 weight percent, based on the weight of the photoconductive layer. The optional second charge transport material, when present, can
30 be in an amount of at least about 2 weight percent, in other embodiments from about 2.5 to about 25 weight percent, based on the weight of the photoconductive layer, and in

further embodiments in an amount from about 4 to about 20 weight percent, based on the weight of the photoconductive layer. The binder is in an amount from about 15 to about 80 weight percent, based on the weight of the photoconductive layer, and in further embodiments in an amount from about 20 to about 75 weight percent, based on the weight of the photoconductive layer. A person of ordinary skill in the art will recognize that additional ranges within the explicit ranges of compositions are contemplated and are within the present disclosure.

For the dual layer embodiments with a separate charge generating layer and a charge transport layer, the charge generation layer generally comprises a binder in an amount from about 10 to about 90 weight percent, in further embodiments from about 15 to about 80 weight percent and in some embodiments in an amount from about 20 to about 75 weight percent, based on the weight of the charge generation layer. The optional charge transport material in the charge generating layer, if present, generally can be in an amount of at least about 2.5 weight percent, in further embodiments from about 4 to about 30 weight percent and in other embodiments in an amount from about 10 to about 25 weight percent, based on the weight of the charge generating layer. The charge transport layer generally comprises a binder in an amount from about 20 weight percent to about 70 weight percent and in further embodiments in an amount from about 30 weight percent to about 50 weight percent. A person of ordinary skill in the art will recognize that additional ranges of binder concentrations for the dual layer embodiments within the explicit ranges above are contemplated and are within the present disclosure.

For the embodiments with a single layer having a charge generating compound and a charge transport material, the photoconductive layer generally comprises a binder, a charge transport material, and a charge generation compound. The charge generation compound can be in an amount from about 0.05 to about 25 weight percent and in further embodiment in an amount from about 2 to about 15 weight percent, based on the weight of the photoconductive layer. The charge transport material can be in an amount from about 10 to about 80 weight percent, in other embodiments from about 25 to about 65 weight percent, in additional embodiments from about 30 to about 60 weight percent and in further embodiments in an amount from about 35 to about 55 weight percent, based on the weight of the photoconductive layer, with the remainder of the photoconductive layer

comprising the binder, and optionally additives, such as any conventional additives. A single layer with a charge transport composition and a charge generating compound generally comprises a binder in an amount from about 10 weight percent to about 75 weight percent, in other embodiments from about 20 weight percent to about 60 weight
5 percent, and in further embodiments from about 25 weight percent to about 50 weight percent. Optionally, the layer with the charge generating compound and the charge transport material may comprise a second charge transport material. The optional second charge transport material, if present, generally can be in an amount of at least about 2.5 weight percent, in further embodiments from about 4 to about 30 weight percent and in
10 other embodiments in an amount from about 10 to about 25 weight percent, based on the weight of the photoconductive layer. A person of ordinary skill in the art will recognize that additional composition ranges within the explicit compositions ranges for the layers above are contemplated and are within the present disclosure.

In general, any layer with an electron transport layer can advantageously further
15 include a UV light stabilizer. In particular, the electron transport layer generally can comprise an electron transport compound, a binder, and an optional UV light stabilizer. An overcoat layer comprising an electron transport compound is described further in copending U.S. Patent Application Serial No. 10/396,536 to Zhu et al. entitled, “Organophotoreceptor With An Electron Transport Layer,” incorporated herein by
20 reference. For example, an electron transport compound as described above may be used in the release layer of the photoconductors described herein. The electron transport compound in an electron transport layer can be in an amount from about 10 to about 50 weight percent, and in other embodiments in an amount from about 20 to about 40 weight percent, based on the weight of the electron transport layer. A person of ordinary skill in
25 the art will recognize that additional ranges of compositions within the explicit ranges are contemplated and are within the present disclosure.

The UV light stabilizer, if present, in any one or more appropriate layers of the photoconductor generally is in an amount from about 0.5 to about 25 weight percent and in some embodiments in an amount from about 1 to about 10 weight percent, based on
30 the weight of the particular layer. A person of ordinary skill in the art will recognize that

additional ranges of compositions within the explicit ranges are contemplated and are within the present disclosure.

For example, the photoconductive layer may be formed by dispersing or dissolving the components, such as one or more of a charge generating compound, the
5 charge transport material of this invention, a second charge transport material such as a charge transport compound or an electron transport compound, a UV light stabilizer, and a polymeric binder in organic solvent, coating the dispersion and/or solution on the respective underlying layer and drying the coating. In particular, the components can be dispersed by high shear homogenization, ball-milling, attritor milling, high energy bead
10 (sand) milling or other size reduction processes or mixing means known in the art for effecting particle size reduction in forming a dispersion.

The photoreceptor may optionally have one or more additional layers as well. An additional layer can be, for example, a sub-layer or an overcoat layer, such as a barrier layer, a release layer, a protective layer, or an adhesive layer. A release layer or a
15 protective layer may form the uppermost layer of the photoconductor element. A barrier layer may be sandwiched between the release layer and the photoconductive element or used to overcoat the photoconductive element. The barrier layer provides protection from abrasion to the underlayers. An adhesive layer locates and improves the adhesion between a photoconductive element, a barrier layer and a release layer, or any
20 combination thereof. A sub-layer is a charge blocking layer and locates between the electrically conductive substrate and the photoconductive element. The sub-layer may also improve the adhesion between the electrically conductive substrate and the photoconductive element.

Suitable barrier layers include, for example, coatings such as crosslinkable
25 siloxanol-colloidal silica coating and hydroxylated silsesquioxane-colloidal silica coating, and organic binders such as polyvinyl alcohol, methyl vinyl ether/maleic anhydride copolymer, casein, polyvinyl pyrrolidone, polyacrylic acid, gelatin, starch, polyurethanes, polyimides, polyesters, polyamides, polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride, polycarbonates, polyvinyl butyral, polyvinyl acetoacetal, polyvinyl formal,
30 polyacrylonitrile, polymethyl methacrylate, polyacrylates, polyvinyl carbazoles, copolymers of monomers used in the above-mentioned polymers, vinyl chloride/vinyl

acetate/vinyl alcohol terpolymers, vinyl chloride/vinyl acetate/maleic acid terpolymers, ethylene/vinyl acetate copolymers, vinyl chloride/vinylidene chloride copolymers, cellulose polymers, and mixtures thereof. The above barrier layer polymers optionally may contain small inorganic particles such as fumed silica, silica, titania, alumina, 5 zirconia, or a combination thereof. Barrier layers are described further in U.S. Patent 6,001,522 to Woo et al., entitled "Barrier Layer For Photoconductor Elements Comprising An Organic Polymer And Silica," incorporated herein by reference. The release layer topcoat may comprise any release layer composition known in the art. In some embodiments, the release layer is a fluorinated polymer, siloxane polymer, 10 fluorosilicone polymer, silane, polyethylene, polypropylene, polyacrylate, or a combination thereof. The release layers can comprise crosslinked polymers.

The release layer may comprise, for example, any release layer composition known in the art. In some embodiments, the release layer comprises a fluorinated polymer, siloxane polymer, fluorosilicone polymer, polysilane, polyethylene, 15 polypropylene, polyacrylate, poly(methyl methacrylate-co-methacrylic acid), urethane resins, urethane-epoxy resins, acrylated-urethane resins, urethane-acrylic resins, or a combination thereof. In further embodiments, the release layers comprise crosslinked polymers.

The protective layer can protect the organophotoreceptor from chemical and 20 mechanical degradation. The protective layer may comprise any protective layer composition known in the art. In some embodiments, the protective layer is a fluorinated polymer, siloxane polymer, fluorosilicone polymer, polysilane, polyethylene, polypropylene, polyacrylate, poly(methyl methacrylate-co-methacrylic acid), urethane resins, urethane-epoxy resins, acrylated-urethane resins, urethane-acrylic resins, or a 25 combination thereof. In some embodiments of particular interest, the release layers are crosslinked polymers.

An overcoat layer may comprise an electron transport compound as described further in copending U.S. Patent Application Serial No. 10/396,536, filed on March 25, 30 2003 to Zhu et al. entitled, "Organoreceptor With An Electron Transport Layer," incorporated herein by reference. For example, an electron transport compound, as described above, may be used in the release layer of this invention. The electron

transport compound in the overcoat layer can be in an amount from about 2 to about 50 weight percent, and in other embodiments in an amount from about 10 to about 40 weight percent, based on the weight of the release layer. A person of ordinary skill in the art will recognize that additional ranges of composition within the explicit ranges are
5 contemplated and are within the present disclosure.

Generally, adhesive layers comprise a film forming polymer, such as polyester, polyvinylbutyral, polyvinylpyrrolidone, polyurethane, polymethyl methacrylate, poly(hydroxy amino ether) and the like. Barrier and adhesive layers are described further in U.S. Patent 6,180,305 to Ackley et al., entitled "Organic Photoreceptors for Liquid
10 Electrophotography," incorporated herein by reference.

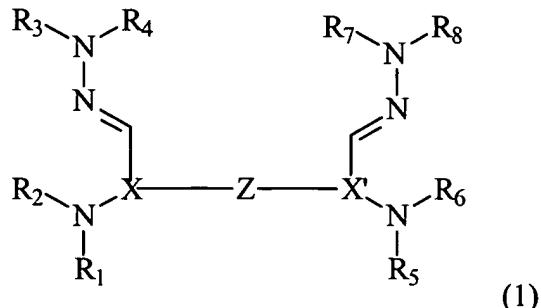
Sub-layers can comprise, for example, polyvinylbutyral, organosilanes, hydrolyzable silanes, epoxy resins, polyesters, polyamides, polyurethanes, and the like. In some embodiments, the sub-layer has a dry thickness between about 20 Angstroms and about 2,000 Angstroms. Sublayers containing metal oxide conductive particles can be
15 between about 1 and about 25 microns thick. A person of ordinary skill in the art will recognize that additional ranges of compositions and thickness within the explicit ranges are contemplated and are within the present disclosure.

The charge transport materials as described herein, and photoreceptors including these compounds, are suitable for use in an imaging process with either dry or liquid
20 toner development. For example, any dry toners and liquid toners known in the art may be used in the process and the apparatus of this invention. Liquid toner development can be desirable because it offers the advantages of providing higher resolution images and requiring lower energy for image fixing compared to dry toners. Examples of suitable liquid toners are known in the art. Liquid toners generally comprise toner particles dispersed in a carrier liquid. The toner particles can comprise a colorant/pigment, a resin binder, and/or a charge director. In some embodiments of liquid toner, a resin to pigment ratio can be from 1:1 to 10:1, and in other embodiments, from 4:1 to 8:1. Liquid toners are described further in Published U.S. Patent Applications 2002/0128349, entitled "Liquid Inks Comprising A Stable Organosol," 2002/0086916, entitled "Liquid Inks
25 Comprising Treated Colorant Particles," and 2002/0197552, entitled "Phase Change
30

Developer For Liquid Electrophotography," all three of which are incorporated herein by reference.

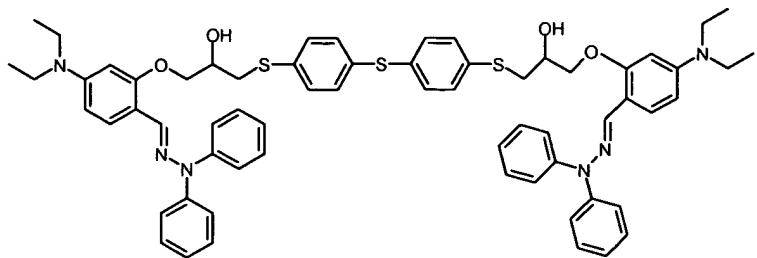
Charge Transport Material

5 As described herein, an organophotoreceptor comprises a charge transport material having the formula

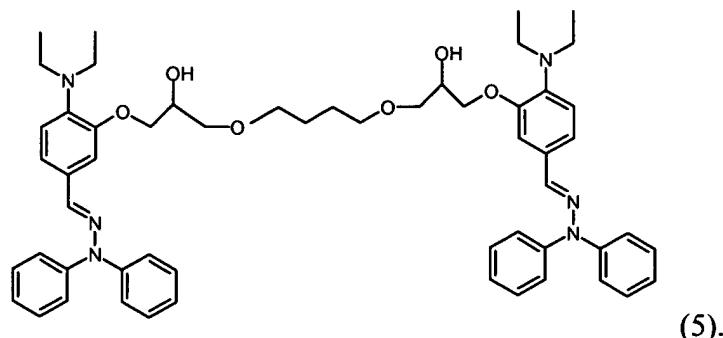
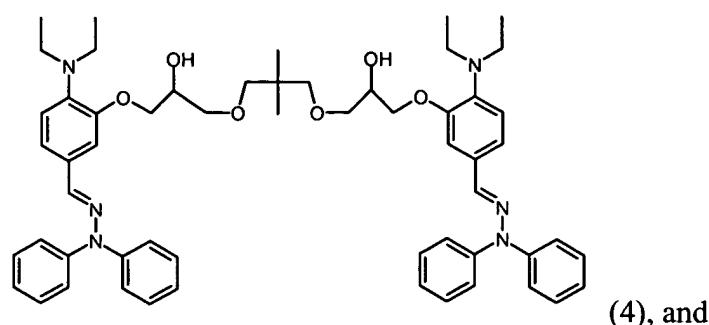
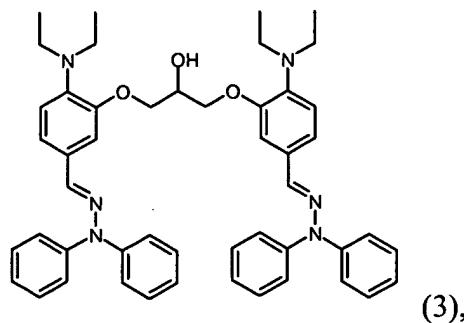


where R₁, R₂, R₃, R₄, R₅, R₆, R₇, and R₈ are, each independently, an alkyl group, an alkaryl group, an aryl group, or heterocyclic group, X and X' are, each independently, aromatic groups, and Z is a divalent linking group having the formula -(CH₂)_m-⁻, branched or linear, where m is an integer between 1 and 30, inclusive, and one or more of the methylene groups may be replaced by O, S, C=O, O=S=O, a heterocyclic group, an aromatic group, urethane, urea, an ester group, a NR₉ group, a CHR₁₀ group, or a CR₁₁R₁₂ group where R₉ and R₁₀ are, each independently, H, hydroxyl, thiol, an alkoxy group, an alkyl group, or an aryl group, and R₁₁, and R₁₂ are, each independently, H, hydroxyl, thiol, an alkoxy group, an alkyl group, an aryl group, or a part of a cyclic ring.

Specific, non-limiting examples of suitable charge transport materials within the general Formula (1) of the present invention have the following structures:



20



5

Similar asymmetric compounds can be formed as described below.

Synthesis Of Charge Transport Materials

10 The synthesis of the charge transport materials of this invention can be prepared by the following multi-step synthetic procedure, although other suitable procedures can be used by a person of ordinary skill in the art based on the disclosure herein.

15 The first step is the preparation of an (N,N-disubstituted)hydrazone of an aromatic aldehyde or ketone having an (N,N-disubstituted)amino group and, on the aromatic ring, either a functional group or a reactive ring group that can react with the functional group.

Non-limiting examples of the functional group are hydroxyl, thiol, and amino group. Non-limiting examples of suitable reactive ring group include epoxy group, thiiranyl group, or aziridino group.

The (N,N-Disubstituted)hydrazone of an aromatic aldehyde or ketone having an (N,N-disubstituted)amino group and a reactive functional group, in addition to the amino group, can be prepared, for example, by the reaction of a corresponding aromatic aldehyde or ketone having a functional group, such as 4-diethylamino-2-hydroxybenzaldehyde, with a corresponding (N,N-disubstituted)hydrazine, such as N,N-diphenylhydrazine, in refluxing ethanol. The reaction can be catalyzed by an appropriate amount of concentrated acid, such as sulfuric acid and hydrochloric acid.

In some embodiments, the (N,N-disubstituted)hydrazone of an aromatic aldehyde or ketone having an (N,N-disubstituted)amino group and a reactive functional group, in addition to the amino group can then react with a first linking compound containing two reactive functional groups, such as diglycidyl ethers (i.e. neopentyl glycol diglycidyl ether and 1,4-butanediol diglycidyl ether), to form a charge transport material, such as Compounds (4) and (5) above. The reaction can be catalyzed by, for example, 4-(dimethylamino)pyridine or triethylamine. The reaction mixture can be refluxed approximately for 15 to 48 hours. After the reaction can be terminated and the product purified by column chromatography.

The first linking compound containing two reactive ring groups can be either commercially obtained or prepared by the epoxidation reaction of the corresponding dialkene compound to form a di-epoxy compound. The di-epoxy compound can also be transformed into a di-thiiranyl compound by refluxing the di-epoxy compound and ammonium thiocyanate in tetrahydrofuran (THF). Such epoxidation reaction is described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York, 1983, pp. 494-498, incorporated herein by reference. The dialkene compound can be prepared by the Wittig reaction between a suitable di-aldehyde or di-keto compound and a suitable Wittig reagent. The Wittig and related reactions are described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York, 1983, pp. 69-77, incorporated herein by reference.

In some embodiments, the (N,N-disubstituted)hydrazone of an aromatic aldehyde or ketone having an (N,N-disubstituted)amino group and a functional group can react with an organic compound containing one reactive ring group, such as an epoxy group, a thiiranyl group, or an aziridino group, to form an (N,N-disubstituted)hydrazone of an aromatic aldehyde or ketone having an (N,N-disubstituted)amino group and a reactive ring group. Non-limiting examples of suitable organic compound comprising an epoxy group for this invention are epihalohydrins (i.e. epichlorohydrin) and diglycidyl ethers (i.e. neopentyl glycol diglycidyl ether and 1,4-butanediol diglycidyl ether). The organic compound comprising an epoxy group can also be prepared by the epoxidation reaction of the corresponding alkene. Such epoxidation reaction is described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York, 1983, pp. 494-498, incorporated herein by reference. The alkene can be prepared by the Wittig reaction between a suitable aldehyde or keto compound and a suitable Wittig reagent. The Wittig and related reactions are described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York, 1983, pp. 69-77, incorporated herein by reference. The thiiranyl compound can be obtained by reacting the corresponding epoxy compound with ammonium thiocyanate in refluxing tetrahydrofuran (THF).

The (N,N-disubstituted)hydrazone of an aromatic aldehyde or ketone having an (N,N-disubstituted)amino group and a reactive ring group can then react with a second linking compound containing two functional groups to form a charge transport material of this invention, such as Compound (2). Non-limiting examples of suitable second linking compound are dihydroxyl compounds (i.e. 2,2'-bi-7-naphtol, 1,4-dihydroxybenzene, 1,3-dihydroxybenzene, 10,10-bis(4-hydroxyphenyl) anthrone, 4,4'-sulfonyldiphenol, bisphenol, 4,4'-(9-fluorenylidene)diphenol, 1,10-decanediol, 1,5-pentanediol, diethylene glycol, 4,4'-(9-fluorenylidene)-bis(2-phenoxyethanol), bis(2-hydroxyethyl) terephthalate, bis[4-(2-hydroxyethoxy)phenyl] sulfone, hydroquinone-bis(2-hydroxyethyl)ether, and bis(2-hydroxyethyl) piperazine), dithiol compounds (i.e. 4,4'-thiobisbenzenethiol, 1,4-benzenedithiol, 1,3-benzenedithiol, sulfonyl-bis(benzenethiol), 2,5-dimercapto-1,3,4-thiadiazole, 1,2-ethanedithiol, 1,3-propanedithiol, 1,4-butanedithiol, 1,5-pentanedithiol, and 1,6-hexanedithiol), and diamino compounds (i.e. diaminoarenes,

and diaminoalkanes). All of the above examples of dihydroxyl compounds, dithiol compounds, and diamino compounds are commercially available. The reaction can be carried out in a solvent, such as butanone, and in the presence of triethylamine at room temperature. After the reaction can be terminated, the product is purified by column chromatography.

In some embodiments, the (N,N-disubstituted)hydrazone of an aromatic aldehyde or ketone having an (N,N-disubstituted)amino group and a functional group can react with the (N,N-disubstituted)hydrazone of an aromatic aldehyde or ketone having an (N,N-disubstituted)amino group and a reactive ring group to form a charge transport material of this invention, such as Compound (3). The reaction condition is that a base such as triethylamine is added as a catalyst. The reaction mixture is refluxed approximately for 6 to 48 hours. After the reaction is terminated, the product is purified by column chromatography.

For the formation of an asymmetric compound, the linking compound can be reacted with two different (N,N-disubstituted)hydrazones bonded with an aromatic group, either sequentially or simultaneously. The reaction conditions can be selected to encourage the formation of the asymmetric compound, such as the sequential reaction with a greater than stoichiometric amount of the linking compound used in the first sequential reaction. To the extent that a mixture of symmetric and asymmetric compounds is formed, the different compounds can be separated from each other, for example, with chromatographic techniques. Similarly, asymmetric linking compounds can be used to form the asymmetric compounds.

While the linking reactions for connecting the linking compound with the aromatic hydrazone compound(s) described above are based on ring opening reactions with reactive ring groups, such as epoxy groups, thiiranyl groups and/or aziridino groups, other linking reactions can be used. Generally, any addition reactions known in the art can be adapted for connecting the linking compound to the aromatic hydrazones. For example, reactions that form esters or the like can be used to join a hydroxyl group with a carboxylic acid group.

The invention will now be described further by way of the following examples.

EXAMPLES

Example 1 - Synthesis And Characterization Charge Transport Materials

This example described the synthesis and characterization of Compounds 2-5 in which the numbers refer to formula numbers above. The characterization involves both
5 chemical characterization and the electronic characterization of materials formed with the compound.

4-Diethylamino-2-hydroxybenzaldehyde N,N-diphenylhydrazone

A solution of N,N-diphenylhydrazine hydrochloride (79.5 g, 0.36 mol, from
10 Aldrich, Milwaukee, WI) in ethanol (500 ml) was slowly added to a solution of 4-diethylamino-2-hydroxybenzaldehyde (58.0 g, 0.3 mol, from Aldrich, Milwaukee, WI) in ethanol (500 ml) in the presence of excess sodium carbonate. The reaction mixture was refluxed until all of the aldehyde reacted in about 1/2 hour. The residue obtained after evaporation of the solvent (800 ml) was treated with ether, and the ether extract was
15 washed with water until the pH of the water reached 7. The organic layer was dried over anhydrous magnesium sulphate, treated with activated charcoal, and filtered. Then, the ether solvent was evaporated. The residue was recrystallized from ethanol. Crystalline 4-diethylamino-2-hydroxybenzaldehyde N,N-diphenylhydrazone was filtered off and washed with cold ethanol. The yield was 85 g (78.8 %). The melting point was found to
20 be 95.5-96.5 °C (recrystallized from a mixture of 2-propanol and ether in a 10:1 ratio by volume). The ¹H NMR spectrum (100 MHz) of the product in CDCl₃ was characterized by the following chemical shifts (δ , ppm): 11.55 (s, 1H, OH); 7.55-6.95 (m, 11H, CH=N, Ph); 6.7 (d, J =8.6 Hz; 1H, 6-H of 1,2,4-subst. Ph); 6.23 (s, 1H, 3-H of 1,2,4-subst. Ph); 6.1 (d, J =8.6 Hz, 1H, 5-H of 1,2,4-subst. Ph); 3.3 (q, J =8.0 Hz, 4H, CH₂); 1.1 (t, J =8.0 Hz, 6H, CH₃). An elemental analysis yielded the following results in weight percent C
25 76.68, H 7.75, and N 11.45, which compared with calculated values for C₂₃H₂₅N₃O in weight percent of C 76.85, H 7.01, and N 11.69.

4-Diethylamino-2-(1,2-epoxypropoxy)benzaldehyde N,N-diphenylhydrazone

A mixture of the 4-diethylamino-2-hydroxybenzaldehyde N,N-diphenylhydrazone (10.0 g, 27.82 mmol, prepared as described above), 85 % powdered potassium hydroxide (3.7 g, 0.05 mol), and anhydrous sodium sulfate (1.4 g, 11.13 mmol) in 35 ml of epichlorohydrin (commercially obtained from Aldrich, Milwaukee, WI) was stirred vigorously at 30-35 °C until the 4-diethylamino-2-hydroxybenzaldehyde N,N-diphenylhydrazone disappeared (2.5 hours, as determined by thin layer chromatography (TLC)). After termination of the reaction by cooling the mixture to room temperature, the mixture was diluted with diethyl ether, and washed with copious amounts of water until the washed water reached a pH value of 7. The organic layer was dried over anhydrous magnesium sulfate, treated with activated charcoal, and filtered. The diethyl ether and unreacted epichlorohydrin were removed by evaporation under a vacuum. The crystals formed upon standing at room temperature were filtered off and washed with 2-propanol to give 9.0 g (77.6 %) of the desired compound. The melting point was found to be 86-87 °C (recrystallized from 10:1 v/v of 2-propanol:ether mixture). The ¹H NMR spectrum (100 MHz) of the product in CDCl₃ was characterized by the following chemical shifts (δ , ppm): 8.0 (d, 1H, 6-H of 1,2,4-subst. Ph); 7.8-7.0 (m, 11H, CH=N, Ph); 6.45 (d, 1H, 5-H of 1,2,4-subst. Ph); 6.1 (s, 1H, 3-H of 1,2,4-subst. Ph); 4.35-3.75 (m, 2H, OCH₂); 3.35 (q, 4H, CH₂); 3.05 (p, 1H, CH); 3.65 (t, 1H, one of CH₂ of oxirane); 2.45 (dd, 1H, one of CH₂ of oxirane); 1.15 (t, 6H, CH₃). Elemental analysis yielded the following values in weight percent C 74.95, H 6.88, and N 9.92, which compared with calculated values for C₂₆H₂₉N₃O₂ in weight percent of C 75.15, H 7.03, and N 10.11.

Compound (2)

Triethylamine (TEA) (0.5 ml, 3.58 mmol, from Aldrich, Milwaukee, WI) was slowly added to a solution of 8.7 g (21.0 mmol) of 4-diethylamino-2-(1,2-epoxypropoxy)benzaldehyde N,N-diphenylhydrazone (prepared as described above) and 2.5 g (10.0 mmol) of 4,4'-thiobisbenzenethiol (from Aldrich, Milwaukee, WI) in 25 ml of 2-butanone, while the temperature of the reaction mixture was maintained below 30 °C. The reaction mixture was maintained at room temperature overnight. After the

solvent was evaporated under a vacuum, the residue was subjected to column chromatography with a mixture of propanone and hexane in a ratio of 1:4 by volume. The fractions containing Compound (2) were collected. After the removal of the solvent, an oily residue was obtained and then dissolved in 30 ml of a mixture of 2-propanol and ether in a ratio of 2:1 by volume. The solution was cooled to 5 °C and crystals were formed upon standing. The crystals were filtered off and washed with 2-propanol to give 7.2 g (67.5 %) of Compound (2). The melting point was found to be 147.5-151.5 °C (recrystallized from a mixture of 2-propanol and ether in a ratio of 10:1 by volume). The ¹H NMR spectrum (100 MHz) of the product in CDCl₃ was characterized by the following chemical shifts (δ , ppm): 7.7 (d, 2H, 6-H of 1,2,4-subst. Ph); 7.6-6.9 (m, 30H, CH=N, Ar); 6.35 (d, 2H, 5-H of 1,2,4-subst. Ph); 6.0 (s, 2H, 3-H of 1,2,4-subst. Ph); 4.0 (m, 6H, OCH₂CH); 3.3 (q, 8H, CH₂CH₃); 2.9 (m, 4H, CH₂S); 2.3 (s, 2H, OH); 1.1 (t, 12H, CH₃). An elemental analysis yielded the following results in weight percent C 70.95, H 5.21, and N 7.92, which compared to calculated values for C₆₄H₅₆N₆O₄S₃ in weight percent of C 71.88, H 5.28, and N 7.86.

Compound (3)

A 0.6 ml (4.45 mmol) quantity of triethylamine (TEA) was added to a mixture of 4-diethylamino-2-hydroxybenzaldehyde N,N-diphenylhydrazone (4.0 g, 11.13 mmol, prepared as described above) and 4-diethylamino-2-(1,2-epoxypropoxy)benzaldehyde N,N-diphenylhydrazone (4.62 g, 11.13 mmol, prepared as described above) in 15 ml of 2-butanone. The mixture was refluxed until one of the starting compounds disappeared, in approximately 38 hours. At the end of the reaction, 2-butanone and TEA were distilled off, and the residue was subjected to chromatography using a column packed with silica gel (Merck grade 9385, commercially available from Aldrich) and a mixture of hexane and propanone in a ratio of 4:1 by volume as the eluant. The fractions containing Compound (3) were collected. Compound (3) was isolated and the yield was 6.7 g (77.7 %); The melting point was found to be 179-180 °C (recrystallized from toluene). The ¹H NMR spectrum (100 MHz) of the product in CDCl₃ was characterized by the following chemical shifts (δ , ppm): 7.87 (d, $J=8.8$ Hz; 2H, 6-H of 1,2,4-subst. Ph); 7.45

(s, 2H, CH=N); 7.41-6.98 (m, 26H, Ar); 6.39 (d, $J=8.7$ Hz; 2H, 5-H of 1,2,4-subst. Ph); 6.02 (s, 2H, 3-H of 1,2,4-subst. Ph); 3.89 (m, 1H, CH_2CHCH_2); 3.82-3.69 (m, 4H, CH_2CHCH_2); 3.36 (q, $J=7.1$ Hz; 4H CH_2CH_3); 2.13 (d, $J=6.0$ Hz; 1H, OH); 1.16 (t, $J=6.9$ Hz; 6H, CH_2CH_3). An elemental analysis yielded the following results in weight percent
5 C 75.75, H 6.98, and N 10.68, which compared to calculated values for $\text{C}_{49}\text{H}_{54}\text{N}_6\text{O}_3$ in weight percent of C 75.94, H 7.02, and N 10.84.

Compound (4)

A mixture of 4-diethylamino-2-hydroxybenzaldehyde N,N-diphenylhydrazone
10 (6.18 g, 17.2 mmol, prepared as described above) and neopentyl glycol diglycidyl ether (1.86 g, 8.6 mmol, from Aldrich, Milwaukee, WI) was heated at 110-115 °C for 15 hours in the presence of catalyst 4-(dimethylamino)pyridine (0.55 g, 4.5 mmol, from Aldrich, Milwaukee, WI). The product was isolated by subjecting the reaction mixture to column chromatography (silica gel, grade 62, 60-200 mesh, 150 Å, Aldrich) using a mixture of acetone and hexane in a 1:4 ratio by volume as the eluant. Compound (4) was obtained
15 as an oil with a yield of 4.5 g (56.2 %). The ^1H NMR spectrum (100 MHz) of the product in CDCl_3 was characterized by the following chemical shifts (δ in ppm): 7.8 (d, 2H, 6-H of 1,2,4-subst. Ph); 7.6-6.9 (m, 22H, CH=N, Ph); 6.3 (d, 2H, 5-H of 1,2,4-subst. Ph); 6.0 (s, 2H, 3-H of 1,2,4-subst. Ph); 4.0-3.0 (m, 22H, NCH_2CH_3 ,
20 $\text{OCH}_2\text{CHCH}_2\text{OCH}_2$); 2.45 (s (br), 2H, OH); 1.1 (t, 12H, CH_3); 0.8 (s, 6H, $\text{C}(\text{CH}_3)_2$). An elemental analysis yielded the following results in weight percent C 73.02, H 7.38, and N 8.92, which compared to calculated values for $\text{C}_{57}\text{H}_{70}\text{N}_6\text{O}_6$ in weight percent of C 73.21, H 7.54, and N 8.99.

Compound (5)

4-Diethylamino-2-(hydroxy)benzaldehyde N,N-diphenylhydrazone (5.6 g, 15.6 mmol, prepared as described above) and 1,4-butanediol diglycidyl ether (1.58g, 7.8 mmol, from Aldrich, Milwaukee, WI) were dissolved in 15ml of methylethylketone, and 0.8 ml of triethylamine was added to the solution. The mixture was refluxed for 48 hours. After
30 evaporation of the solvent, the residue was purified by column chromatography (silica gel, grade 62, 60-200 mesh, 150 Å, Aldrich) using a mixture of acetone and hexane in a 1:4

ratio by volume as the eluant. The yield of Compound (5) was 4.8 g (66.7%). The melting point was found to be 125.5-126.5°C (recrystallized from toluene). The ¹H NMR spectrum (100 MHz) of the product in CDCl₃ was characterized by the following chemical shifts (δ , ppm): 7.8 (d, 2H, 6-H of 1,2,4-subst.Ph); 7.6-6.9 (m, 22H, CH=N, Ph); 5 6.3 (d, 2H, 5-H of 1,2,4-subst. Ph); 6.0 (s, 2H, 3-H of 1,2,4-subst. Ph); 4.0-3.0 (m, 22H, NCH₂CH₃, OCH₂CHCH₂OCH₂); 2.35 (m, 2H, 2x OH); 1.5 (m, 4H, OCH₂(CH₂)₂CH₂O); 1.1 (t, 12H, CH₃). An elemental analysis yielded the following results in weight percent C 73.22, H 6.88, and N 9.02, which compared to calculated values for C₅₆H₆₄N₆O₆in weight percent of C 73.34, H 7.03, and N 9.16.

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Example 2 - Charge Mobility Measurements

This example describes the measurement of charge mobility for charge transport materials, specifically Compounds (2) - (5) above.

Sample 1

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A mixture of 0.1 g of the Compound (2) and 0.1 g of polyvinylbutyral (S-LEC B BX-1, from Sekisui Chemical, Japan) was dissolved in 2 ml of tetrahydrofuran (THF). The solution was coated on the polyester film with conductive Al layer by the dip roller method. After drying for 1 h at 80 °C, a clear 10 μ m thick layer was formed.

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Sample 2

A mixture of 0.1 g of the Compound (3) and 0.1 g of polyvinylbutyral (S-LEC B BX-1, from Sekisui Chemical, Japan) was dissolved in 2 ml of THF. The solution was coated on the polyester film with conductive Al layer by the dip roller method. After drying for 1 h at 80 °C, a clear 10 μ m thick layer was formed.

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Sample 3

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A mixture of 0.1 g of the Compound (4) and 0.1 g of polyvinylbutyral (S-LEC B BX-1, from Sekisui Chemical, Japan) was dissolved in 2 ml of THF. The solution was coated on the polyester film with conductive Al layer by the dip roller method. After drying for 1 h at 80 °C, a clear 10 μ m thick layer was formed.

Sample 4

A mixture of 0.1 g of the Compound (5) and 0.1 g of polyvinylbutyral (S-LEC B BX-1, from Sekisui Chemical, Japan) was dissolved in 2 ml of THF. The solution was coated on the polyester film with conductive Al layer by the dip roller method. After drying for

5 1 h at 80 °C, a clear 10 µm thick layer was formed.

Mobility Measurements

Each sample was corona charged positively up to a surface potential U and illuminated with 2 ns long nitrogen laser light pulse. The hole mobility μ was determined

10 as described in Kalade et al., "Investigation of charge carrier transfer in electrophotographic layers of chalkogenide glasses," Proceeding IPCS 1994: The Physics and Chemistry of Imaging Systems, Rochester, NY, pp. 747-752, incorporated herein by reference. The hole mobility measurement was repeated with appropriate changes to the charging regime to charge the sample to different U values, which corresponded to
15 different electric field strength inside the layer E. This dependence on electric field strength was approximated by the formula

$$\mu = \mu_0 e^{\alpha\sqrt{E}}$$

Here E is electric field strength, μ_0 is the zero field mobility and α is Pool-Frenkel parameter. Table 1 lists the mobility characterizing parameters μ_0 and α values and the
20 mobility value at the 6.4×10^5 V/cm field strength as determined by these measurements for the four samples.

Table 1.

Sample	μ_0 (cm ² /V·s)	μ (cm ² /V·s) at $6.4 \cdot 10^5$ V/cm	α (cm/V) ^{0.5}	Ionization Potential (eV)
1 (Compound 2)	$3.2 \cdot 10^{-9}$	$1.6 \cdot 10^{-7}$	0.0049	5.28
2 (Compound 3)	$1.8 \cdot 10^{-8}$	$1.1 \cdot 10^{-6}$	0.0051	5.16
3 (Compound 4)	$4.4 \cdot 10^{-9}$	$2.4 \cdot 10^{-7}$	0.0050	5.23
4 (Compound 5)	$6.7 \cdot 10^{-9}$	$4.6 \cdot 10^{-7}$	0.0053	5.22

Example 3 - Ionization Potential Measurements

This example describes the measurement of the ionization potential for Compounds (2)-(5) described in Example 1.

5 To perform the ionization potential measurements, a thin layer of charge transport material about 0.5 μm thickness was coated from a solution of 2 mg of charge transport material in 0.2 ml of tetrahydrofuran on a 20 cm^2 substrate surface. The substrate was polyester film with an aluminum layer over a methylcellulose sublayer of about 0.4 μm thickness.

10 Ionization potential was measured as described in Grigalevicius et al., "3,6-Di(N-diphenylamino)-9-phenylcarbazole and its methyl-substituted derivative as novel hole-transporting amorphous molecular materials," *Synthetic Metals* **128** (2002), p. 127-131, incorporated herein by reference. In particular, each sample was illuminated with monochromatic light from the quartz monochromator with a deuterium lamp source. The 15 power of the incident light beam was $2\text{-}5\cdot10^{-8}$ W. A negative voltage of -300 V was supplied to the sample substrate. A counter-electrode with the 4.5×15 mm^2 slit for illumination was placed at 8 mm distance from the sample surface. The counter-electrode was connected to the input of a BK2-16 type electrometer, working in the open 20 input regime, for the photocurrent measurement. A $10^{-15} - 10^{-12}$ amp photocurrent was flowing in the circuit under illumination. The photocurrent, I, was strongly dependent on the incident light photon energy $h\nu$. The $I^{0.5}=f(h\nu)$ dependence was plotted. Usually, the dependence of the square root of photocurrent on incident light quanta energy is well described by linear relationship near the threshold (see references "Ionization Potential of Organic Pigment Film by Atmospheric Photoelectron Emission Analysis," *Electrophotography*, 28, Nr. 4, p. 364 (1989) by E. Miyamoto, Y. Yamaguchi, and M. Yokoyama; and "Photoemission in Solids," *Topics in Applied Physics*, **26**, 1-103 (1978) by M. Cordona and L. Ley, both of which are incorporated herein by reference). The 25 linear part of this dependence was extrapolated to the $h\nu$ axis, and the I_p value was determined as the photon energy at the interception point. The ionization potential

measurement has an error of ± 0.03 eV. The ionization potential values are given in Table 1 above.

As understood by those skilled in the art, additional substitution, variation among substituents, and alternative methods of synthesis and use may be practiced within the scope and intent of the present disclosure of the invention. The embodiments above are intended to be illustrative and not limiting. Additional embodiments are within the claims. Although the present invention has been described with reference to particular embodiments, workers skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the invention.

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